Strain modulation of transport criticality in heterogeneous solids

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A vast class of disordered conducting-insulating compounds close to the percolation threshold is characterized by nonuniversal values of transport critical exponents. The lack of universality implies that critical indexes may depend on material properties such as the particular microstructure or the nature of the constituents, and that in principle they can be influenced by suitable applied perturbations leading to important informations about the origin of nonuniversality. Here we show that in RuO$_2$-glass composites the nonuniversal exponent can be modulated by an applied mechanical strain, signaled by a logarithmic divergence of the piezoresistive response at the percolation threshold. We interpret this phenomenon as being due to a tunneling-distance dependence of the transport exponent, supporting therefore a theory of transport nonuniversality proposed some years ago.

Transport properties of disordered insulator-conductor composites are characterized by the existence of a percolation critical value x_c of the conducting phase volume concentration x below which the system becomes an insulator. As $x - x_c \to 0$ the resistivity ρ of the composite diverges by following a power-law behavior of the form:

$$\rho \simeq \rho_0 (x - x_c)^{-t}, \qquad (1)$$

where ρ_0 is a material-dependent prefactor and t is the transport critical exponent[1, 2]. According to the standard theory of transport in isotropic percolating materials, ρ_0 and x_c depend on microscopic details such as the microstructure and the mean inter-grain junction resistivity while, on the contrary, the exponent t is material independent and takes on the value $t \simeq 2.0$ for three dimensional systems[1, 2]. This universal value is indeed observed in a great variety of composites[3, 4, 5, 6] and it is confirmed to a rather high accuracy by calculations on random resistor networks models[7].

Universality of DC transport is understood as being due to the unimportance of microscopic details for the flow of current compared to the topological properties of the percolating backbone[1]. This concept applies also to other transport-percolation phenomena such as for example proton conductivity in biological materials and laminar fluid flows through porous media[8]. Yet, a vast class of disordered composites deviates from universality by displaying values of t larger than 2.0[6, 9] and as high as $t \simeq 7.0$[10] or even more[11]. The lack of universality indicates that the exponent t acquires an additional dependence upon some microscopic properties and variables, whose identification would permit to unveil the mechanisms leading to $t \neq 2.0$. A practical route to achieve this goal is to apply an external perturbation to a nonuniversal composite with the hope of affecting the same microscopic variables which govern nonuniversality. In this case, the applied perturbation would change the value of the critical exponent t.

We have applied this idea to RuO$_2$-glass composites prepared as thick-film resistors (TFRs) in our laboratory. RuO$_2$ as well as other ruthenate (Pb$_2$Ru$_2$O$_6$, Bi$_2$Ru$_2$O$_7$) or oxide (IrO$_2$) TFRs are ideal systems for our study because they display universal ($t \simeq 2.0$) or nonuniversal ($t > 2.0$[6] up to about $t \simeq 7.0$[10]) behavior of transport depending on the microstructure and fabrication procedures, with a good reproducibility and high stability. In these composites, the conducting particles are separated by nanometer-thick film of glass[12] and the dominant mechanism of transport is via quantum tunneling through the glass films[12, 13, 14]. Here we show that when transport is nonuniversal, the critical exponents of our samples can be modified by an applied mechanical strain ε, providing evidence that the microscopic variable governing nonuniversality is the mean tunneling distance a between adjacent conducting grains.

Our samples were prepared by mixing two series of RuO$_2$ powders with 40 nm and 400 nm grain sizes, respectively, with a lead-borosilicate glass powder [PbO(75% wt)-B$_2$O$_3$(10% wt)-SiO$_2$ (15% wt)] of $1-5$ μm grain sizes together with a vehicle of terpineol and ethyl cellulose. 2% of Al$_2$O$_3$ were added to the pastes in order to avoid crystallization. The pastes were screen printed on Al$_2$O$_3$ substrates with gold electrical contacts and fired for 15 minutes at temperatures T_f (see Table I) higher then the temperature of fusion of the glass (about 500°C). The resulting films were about 10 μm thick and several resistivity measurements were taken over eight different samples for each RuO$_2$ volume fraction value.

In Fig.1 we report the room temperature resistivity ρ measured for four different series of TFRs (see Table I) as functions of the RuO$_2$ volume concentration x. As shown in Fig.1(a), resistivity diverges at rather small values of x, as expected when the mean grain size of the conducting phase (40 nm and 400 nm) is smaller than that of the glass (1-5 μm)[15]. The same data are re-plotted in the ln-ln plot of Fig.1(b) together with the corresponding fits
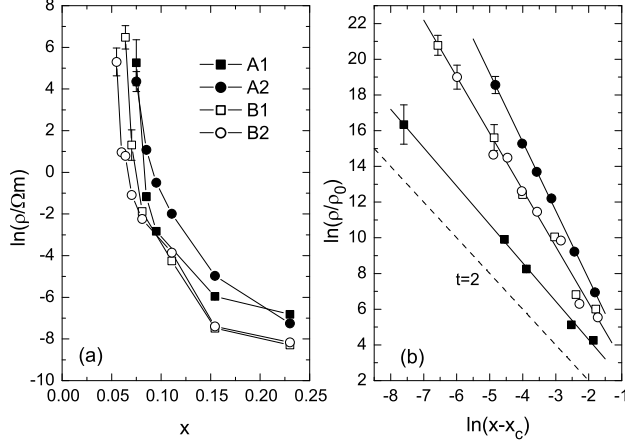
FIG. 1: (a): resistivity ρ as a function of RuO_2 volume concentration x for four different series of TFRs. The solid lines are a guide to the eyes. (b) ln-ln plot of the same data of (a) with fits to Eq.(1) shown by solid lines. The dashed line has slope $t = 2$ corresponding to universal behavior of transport. The prefactor ρ_0, critical concentration x_c and transport exponent t values obtained by the fits are reported in Table I

FIG. 2: (a) relative variation of resistivity as a function of applied strain ε in cantilever bar measurements of the A2 series for different contents x of RuO_2. The solid lines are linear fits to the data. (b) isotropic piezoresistivity response $\Gamma = d \ln(\rho)/d\varepsilon$ obtained from the slopes of (a) as a function of the volume concentration x for the TFRs series of Fig.1.

to Eq.(1) (solid lines) and the best-fit parameters ρ_0, x_c and t are reported in Table I . As it is clearly shown, our resistivity data follow the power law behavior of Eq.(1) with exponent t close to the universal value $t \simeq 2.0$ for the A1 series ($t = 2.15 \pm 0.06$) or markedly nonuniversal as for the A2 case which displays $t = 3.84 \pm 0.06$. The B1 and B2 series have virtually equal values of t ($t \simeq 3.16$) falling in between those of the A1 and A2 series.

The effect of an applied strain ε on transport is obtained by recording the piezoresistive response, *i. e.* the relative resistivity change $\Delta\rho/\rho$ upon applied mechanical strain deformation, by cantilever bar measurements. The RuO_2-glass pastes were screen printed on Al_2O_3 cantilever bars 51 mm long, $b = 5$ mm large, and $h = 0.63$ mm thick. The cantilever was clamped at one end and different weights were applied at the opposite end. The resulting substrate strain ε along the main cantilever axis can be deduced from the relation $\varepsilon = 6Mgd/(Ebh^2)$, where $d = 27.8$ mm is the distance between the resistor and the point of applied force, $E = 332.6$ GPa is the reduced Al_2O_3 Young modulus, g is the gravitational acceleration and M is the value of the applied weight. As shown in Refs.16, 17, from measurements of the longitudinal ($\Delta\rho_\parallel/\rho$) and transverse ($\Delta\rho_\perp/\rho$) piezoresistive responses obtained by measuring the voltage drops along and perpendicular to the main cantilever axis, respectively, it is possible to extract the isotropic resistive variation defined as $\Delta\rho/\rho = (\Delta\rho_\parallel/\rho + 2\Delta\rho_\perp/\rho)/3$. For the values of RuO_2 content used in this work, $\Delta\rho_\parallel/\rho \simeq \Delta\rho_\perp/\rho$ confirming the vicinity to a percolation threshold[16, 17].
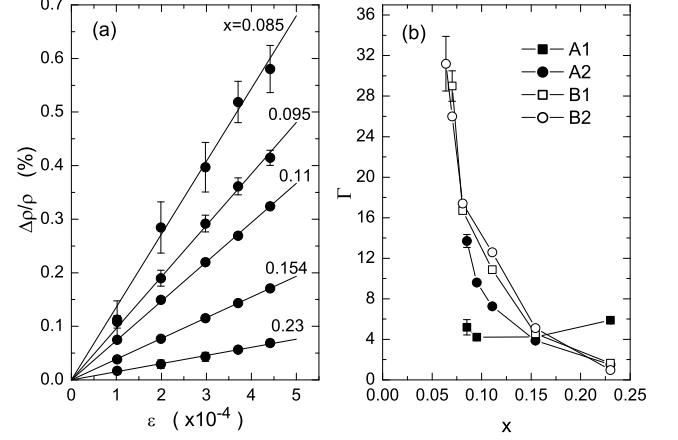
In Fig.2(a) we report $\Delta\rho/\rho$ for various RuO_2 concentrations x of the A2 series as a function of applied strain ε. In the whole range of applied strains, $\Delta\rho/\rho$ changes linearly with ε permitting to extract rather accurate piezoresistive factors $\Gamma = d \ln(\rho)/d\varepsilon$ from the slopes of the linear fits of $\Delta\rho/\rho$ *vs* ε. The so obtained Γ values as a function of x are plotted in Fig.2(b) for the four TFRs series of Fig.1. With the exception of the A1 series, Γ displays a strong dependence upon x and tends to diverge as x approaches to the same critical concentrations x_c at which ρ goes to infinity.

The divergence of Γ at x_c has been reported some years ago[18], but here we show that it is caused by a strain modulation of the critical exponent t. To see this, let us consider Eq.(1) and differentiate it with respect to ε:

$$\frac{d \ln(\rho)}{d\varepsilon} = \Gamma = \Gamma_0 + \frac{d}{d\varepsilon}\left[t \ln\left(\frac{1}{x - x_c}\right)\right]. \qquad (2)$$

Since $\Gamma_0 = d \ln(\rho_0)/d\varepsilon$ is a constant independent of x, all the x dependence of Γ must come from the last term of Eq.(2). However, it must be noted that x is a measure of the concentration p of intergrain junctions with finite resistances present in the sample[1, 2]. In our measurements, the applied strain is only of order 10^{-4}, which is so small that it can eventually change the value of the tunneling junction resistances but cannot modify the concentration p of junctions. So $dx/d\varepsilon$ must be zero and by the same token also $dx_c/d\varepsilon = 0$. Hence the only way to have a x dependence of Γ is to allow the transport exponent t to have non vanishing derivative, which reduces

TABLE I: Label legend of the various sample used in this work with fitting parameters of Eqs.(1,3)

Label	RuO$_2$ grain size	firing temperature T_f	x_c	$\ln(\rho_0/\Omega\mathrm{m})$	t	Γ_0	$dt/d\varepsilon$
A1	400nm	525°C	0.0745	-11.1 ± 0.3	2.15 ± 0.06	5.5 ± 1.5	-0.2 ± 0.4
A2	400nm	600°C	0.0670	-14.2 ± 0.2	3.84 ± 0.06	-8.8 ± 1.6	5.4 ± 0.5
B1	40nm	550°C	0.0626	-14.3 ± 0.5	3.17 ± 0.16	-15.3 ± 3	8.7 ± 0.9
B2	40nm	600°C	0.0525	-13.7 ± 0.7	3.15 ± 0.17	-19.3 ± 2.4	11.0 ± 0.7

Eq.(2) to:

$$\Gamma = \Gamma_0 + \frac{dt}{d\varepsilon} \ln\left(\frac{1}{x - x_c}\right). \tag{3}$$

In Fig.3 we plot the piezoresistive data of Fig.2(b) as a function of $\ln(x - x_c)$ with the same values of the critical concentrations x_c extracted from the resistivity data. Our data fit well with Eq.(3) (solid lines and last two columns of Table I) and indicate that Γ indeed diverges logarithmically as $x \to x_c$ for the series A2, B1, and B2. An analysis of previously published data[18] confirms this conclusion[19]. It is also remarkable that the series A1 has vanishing $dt/d\varepsilon$ within experimental errors, in perfect agreement with the universal value of its exponent ($t \simeq 2.15 \pm 0.06$). We conclude therefore that when the transport exponents of our RuO$_2$ TFRs are nonuniversal, they can be modulated by an applied strain.
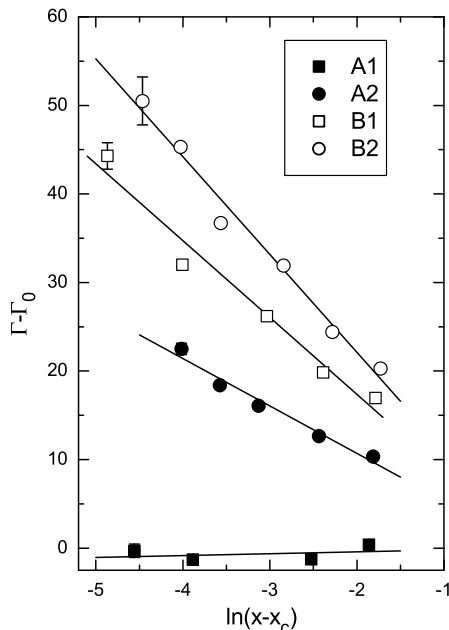

FIG. 3: Piezoresistive factor as a function of $\ln(x - x_c)$ and fits (solid lines) to Eq.(3). The fit parameters $dt/d\varepsilon$ and Γ_0 are reported in Table I. Only sample A1 (solid squares) has quasi-zero slope indicating that $dt/d\varepsilon = 0$.

Let us discuss now what this finding implies in terms of the microscopic origin of nonuniversality. The main effect of the applied strain on the microscopic properties of RuO$_2$-glass composites is that of changing the mean intergrain tunneling distance a, $a \to a(1 + \varepsilon)$, leading to a variation of the microscopic tunneling resistances. Hence, in order to have $dt/d\varepsilon \neq 0$, the transport exponent itself must depend on a. A scenario of this kind has been proposed by Balberg a few years ago in his tunneling-percolation theory of nonuniversality in carbon-black–polymer composites[20]. According to this theory, when the distribution function of the tunneling distance d between two neighboring grains decays with d much slower than the tunneling decay $\exp(-2d/\xi)$, where ξ is the localization length, then the distribution function $h(r)$ of the intergrain tunneling resistances r develops a power-law tail such that $h(r) \propto r^{\alpha-2}$ for $r \to \infty$ where $\alpha = 1 - \xi/(2a)$. It is well known[21] that distribution functions of this kind lead to an explicit dependence of t upon the parameter α[22, 23]:

$$t = \begin{cases} t_0 & \text{if } \nu + \frac{1}{1-\alpha} < t_0 \\ \nu + \frac{1}{1-\alpha} & \text{if } \nu + \frac{1}{1-\alpha} > t_0 \end{cases}, \tag{4}$$

where $t_0 \simeq 2.0$ is the universal transport exponent and $\nu \simeq 0.88$ is the 3D correlation-length exponent. In view of Eq.(4), the term which multiplies the logarithm in Eq.(3) is $dt/d\varepsilon = 1/(1 - \alpha) = 2a/\xi > 0$ when t is given by the second line of Eq.(4) or $dt/d\varepsilon = 0$ when $t = t_0$. However, we note that in RuO$_2$-based TFRs the large difference between the bulk modulus B values of RuO$_2$ and of the glass ($B_{\mathrm{RuO_2}} \simeq 270\mathrm{GPa}$ and $B_{\mathrm{glass}} \simeq 40 - 80\mathrm{GPa}$) leads to local strain variations resulting basically in a strong ε amplification within the softer phase (glass) through which tunneling occurs. Hence, the $dt/d\varepsilon$ values of A2, B1 and B2 reported in Table I are not simply equal to $2a/\xi$ but incorporate also the amplification effect of the strain heterogeneity.

An interesting feature of our piezoresistive data is the change of sign of Γ_0 which from positive for the universal serie A1 becomes negative for the nonuniversal ones (A2,B1 and B2, see Table I). Although being quite surprising at first sight, this result can be naturally explained within the tunneling-percolation model[20]. In fact a tensile strain ($\varepsilon > 0$) enhances the intergrain tunneling resistances leading to an overall enhancement of the sample resistivity, so that $\Gamma = d\ln(\rho)/d\varepsilon$ must be positive. Hence, from Eq.(3), $\Gamma_0 > 0$ when $dt/d\varepsilon = 0$

while when $dt/d\varepsilon > 0$ Γ_0 does not need to be positive to ensure $\Gamma > 0$. Quite remarkably, an effective medium calculation with the tunneling-percolation distribution function $h(r) \propto r^{\alpha-2}$ leads to $\Gamma_0 < 0$ as long as t depends upon α as in the second line of Eq.(4)[19]. This is in agreement with our experimental results (see Table I).

Let us now turn to discuss briefly how other theories of nonuniversality fit our findings. First, the random void model (RVM) of continuum percolation[24] can hardly be applied to the A1 and A2 series, since the RuO_2 particles are not microscopically smaller than the glass grains, so that the conducting phase cannot be regarded as a continuum. In addition, the RVM predicts that t follows Eq.(4) with $\alpha = \alpha_{RVM}$ being a purely topological quantity defined by the distribution of the narrow necks bounded by three interpenetrating insulating spheres. Hence, α_{RVM} is insensitive to an applied strain so that $dt/d\varepsilon = 0$ and the piezoresistivity Γ cannot develop a logarithmic divergence. We exclude also the possibility that our nonuniversal samples are in the mean-field regime for which $t = t_{mf} = 3$[25]. In fact the A2 series has a critical exponent clearly larger than t_{mf} and, more importantly, $dt_{mf}/d\varepsilon$ is expected to be strictly zero.

In summary, we have shown that the piezoresistive response of disordered RuO_2-glass composites has a logarithmic divergence at the percolation threshold when DC transport is nonuniversal. A coherent interpretation of this result calls into play a mean tunneling distance dependence of the resistivity exponent, in agreement with a tunneling-percolation origin of nonuniversality proposed some time ago[20]. Such mechanism of universality breakdown could apply also to other materials for which transport is governed by tunneling such as carbon-black–polymer composites, and experiments on their piezoresistive response could confirm such conjecture.

Before concluding, it is worth to point out that in addition to the importance of our results concerning the origin of transport nonuniversality in tunneling-percolation materials, the reported logarithmic divergence of Γ has also consequences for applications of Ru-based TFRS in force and pressure sensors. In fact, the efficiency of piezoresistive sensors is measured by the magnitude of Γ. However the logarithmic increase of Γ as $x \to x_c$ is not sufficient to overcome the power-law divergence of the resistance fluctuations. This poses serious limitations regarding the precision of pressure/force detection. An alternative route would be to make use of the amplification effects induced by the local elastic heterogeneities by fabricating

RuO_2-based TFRs with softer insulating phases like low melting temperature glasses or even polymeric hosts.

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